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Rafael Verduzco, Neal Scruggs, Julia A. Kornfield, "Liquid crystalline gels self-assembled from block copolymers," Proc. SPIE 5936, Liquid Crystals IX, 59360H (20 August 2005); doi: 10.1117/12.618477

SPIE.

Event: Optics and Photonics 2005, 2005, San Diego, California, United States

Liquid crystalline gels self-assembled from block copolymers

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ABSTRACT

Self-assembly of coil-SGLCP-coil block copolymers provides a route to model liquid crystalline (LC) gels in concentrations ranging from bulk polymer to gels with as little as 5 wt % polymer in a small-molecule LC host. Triblock copolymers with LC-phobic endblocks associate in a nematic liquid crystal to create crosslinks. An SGLCP midblock allows for solubilization of the network. These materials have a precisely tailored network structure ideal for comparison to theory [1] of liquid crystalline elastomers. In addition, the gel responds readily to external fields since the concentration of polymer can be relatively low. In this report we discuss rheological measurements that demonstrate gelation at low polymer concentrations. We show that the association of the PS blocks at low concentration is driven by the presence of the SGLCP, rather than incompatibility between PS and 5CB. We then discuss the alignment of the gels via shear, magnetic fields, electric fields, and alignment surfaces. Finally, we present results on a distinctive striped texture observed in aligned gels when subjected to an applied electric field or normal force. The exceptional electro-optic and mechano-optic responsiveness of these gels coupled with thermally reversible gelation suggests they would be ideal candidates for use in large-area printable display technology.

Keywords: liquid crystal, gel, nematic, self-assembly, block copolymer, display

1. INTRODUCTION

The intriguing combination of crosslinked polymers with liquid crystals results in what has been referred to as a new state of matter.[2] Termed liquid crystal elastomers, such materials combine the orientational response of liquid crystals with the large strain response of soft rubbers. Due to the ability of these polymeric materials to respond to applied fields, strain, and changes in temperature, they have been studied for their potential application as novel display materials, [3] artificial muscles, [4] optical storage media, [5] and tunable lasers.[6] Each application requires a unique combination of liquid crystal group and polymeric architecture. For artificial muscles, lightly crosslinked side group nematic liquid crystalline polymers (SGLCPs) provide large and reversible shape changes upon heating. For tunable lasers, a chiral liquid crystal attached to a polymer results in a material whose selective reflection can be mechanically tuned. For displays, composite materials in which the stabilizing polymer network is swollen by small molecule liquid crystal are desired to allow for fast reorientation dynamics upon application of an electric field. In each case, synthetic approaches to create LC elastomers and gels have been limited by quenched random disorder, [7] leading to optical heterogeneities and inhomogeneous responses to applied stimuli. Elastomers and gels with well-defined network structures are needed to improve material properties and advance fundamental understanding of these fascinating materials.

2. POLYMER STRUCTURES FOR MODEL LC GELS

Block copolymers with long side-group liquid-crystalline (LC) midblocks (>800 kg/mol) and LC-phobic end-blocks form a physical network that swells readily in a small molecule LC to form nematic gels. Ultralong side-group liquid crystal polymers (SGLCP) are used for the midblock to enable gelation at relatively low concentration (~5% polymer). Using polymer-analogous synthesis we prepare SGLCPs with Mw up to 1,000,000 g/mol and Mw/Mn < 1.3. Similar to

Liquid Crystals IX, edited by Iam-Choon Khoo, Proceedings of SPIE Vol. 5936
(SPIE, Bellingham, WA, 2005) · 0277-786X/05/$15 · doi: 10.1117/12.618477

LC elastomers, an initially unaligned, polydomain gel aligns under applied strain, creating a monodomain that is oriented well enough to generate clear conoscopic figures. At the same time, the presence of small molecule liquid crystal allows for rapid dynamics, comparable to pure small molecule liquid crystal. The materials provide model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock.

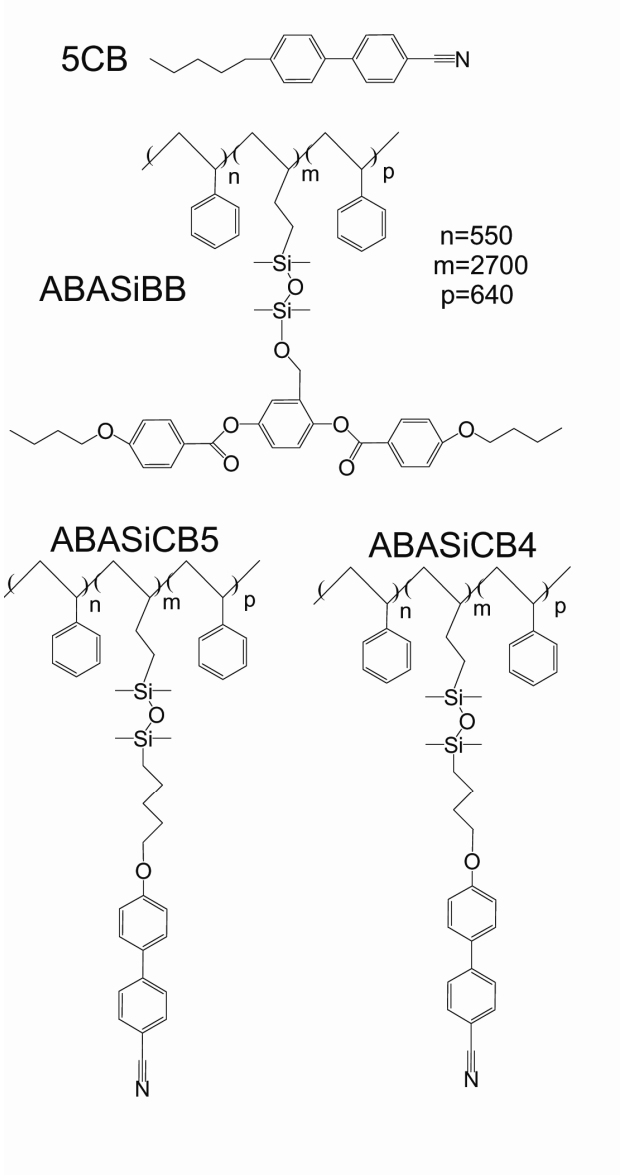

Figure 1: Molecular structure of the nematic solvent 5CB and the ABA triblock liquid crystal polymers. In the naming convention, the ABA prefix denotes a triblock copolymer, Si indicates side groups are attached using siloxane linkers, and mesogen type is denoted by CB for cyanobiphenyl and BB for hydroxybenzoate. The CB polymers are further distinguished by the number of carbons in the alkyl spacer. The analogous homopolymers were also prepared and named PBSiBB, PBSiCB5, and PBSiCB4.

A polymer-analogous approach to synthesis allowed a model series of high-molecular-weight polymers (Figure 1) to be created with different mesogenic types but with the same degree of polymerization. The various mesogenic units were attached to the pendant vinyl groups of 1,2-polybutadiene (1,2 PB) by hydrosilylation. The prepolymer is a 1,2 PB

homopolymer, a diblock copolymer of polystyrene (PS) and 1,2 PB, or a triblock with PS endblocks and a 1,2 PB midblock. Anionic polymerization of the prepolymers confers narrow molar mass distribution. A homologous series of polymers can be produced from a single prepolymer, as illustrated by the triblock copolymers in Figure 1.

Gels are formed by dissolving a triblock copolymer and 5CB in dichloromethane. The mixture is then annealed overnight under vacuum to remove the dichloromethane.

3. PHASE BEHAVIOR

The isotropic transition temperatures of the bulk block copolymers ranged from 40 to 74 ^{o}C (Table 1) and the textures they exhibited, observed using POM, revealed the type of LC order. ABASiCB4 and ABASiBB had textures characteristic of nematic LCs while ABASiCB5 had a rough focal conic texture characteristic of a smectic LC. The presence of a smectic phase in the analogous homopolymer, PBSiCB5, was confirmed by wide-angle x-ray scattering [8]. The type of LC order in each case is consistent with that of the homopolymer analog [8] and with previously established trends for SGLCPs (smaller spacer lengths lead to nematic phases and longer spacer lengths lead to smectic phases) [9]. Similarly side-on SGLCP's are almost always nematic due to the difficulty of a polymer to form smectic layers when both the mesogen and the backbone are parallel to the director [10]. The triblocks consistently have reduced isotropization temperatures relative to their homopolymer analogs. This may be a consequence of the reduced percentage of 1,2-repeat units (88% compared to 98%) in the prepolymer; consequently, the percentage of mesogenic units in the SGLCP midblock (71-84%) is less than that of SGLCP homopolymers (92-94%).

[a]Polymer	[b]Total M_n (kg/mol)	PDI	LC Block M_n (kg/mol)	[c]LC Block % 1,2	[c]LC Block % 1,4	[c]LC Block % Mesogen	[d]T_{ni} (^{o}C)
PB	63	1.04	N/A	~98	~2	N/A	N/A
PBSiBB	743	1.10	712	4	~2	94	120
PBSiCB5	497	1.12		5	~2	93	70
PBSiCB4	467	1.10		6	~2	92	60
[d]ABA	270	1.26	N/A	88	12	N/A	N/A
ABASiBB	1341	1.4	1217	17	12	71	74
ABASiCB5	1172	1.4	1048	4	12	84	64
ABASiCB4	1134	1.4	1010	4	12	84	40

Table 1: Polymer characterization. [a] The polymer names starting with ABA were made from poly[styrene-block-(1,2-butadiene)-block-styrene] triblock copolymer. The polymer names starting with PB were made with 1,2-polybutadiene. Polymers whose name ends with CB5 or CB4 have a cyanobiphenyl mesogen with a 4 or 5 methylene spacer connecting the siloxane group to the mesogen, respectively. Polymers ending with BB have the side-on mesogenic unit (Figure 1). [b] The molar masses of the butadiene pre-polymers were measured using MALLS but the final polymer molar masses listed were calculated based on the fractional conversion of the vinyl groups. [c] The percents are based on the number of monomers in the LC block only. [d] For the ABA triblock copolymers, the two styrene endblocks had molar masses of 57 and 67 kg/mol and the initial 1,2-polybutadiene center block had a molar mass of M_n=146 kg/mol. [d] Nematic to isotropic transition temperature (T_{NI}) of polymers determined using a Zeiss polarized optical microscope (POM) equipped with a Mettler FP82 hot stage.

In solution in 5CB some of the triblock copolymers exhibited biphasic behavior. Mixtures of 5CB with ABASiCB4 exhibited a single sharp transition between the nematic and isotropic phases at all concentrations examined with T_{NI} being slightly depressed (2 ^{o}C or less) relative to pure 5CB. In contrast, mixtures of 5CB with ABASiCB5 at concentrations of 18 wt % or less are biphasic from ambient temperature up to their clearing point with polymer-rich and polymer-poor nematic phases coexisting; at concentrations of 20 wt % or greater there was a single, sharp transition. The tendency to phase separate may be due to the smectic character of this polymer [11]. From this point on we restrict ourselves to single-phase (concentration > 20 wt %) solutions of ABASiCB5. Mixtures of 5CB with

ABASiBB at concentrations less than 10 wt % exhibit a narrow biphasic window with isotropic and nematic phases coexisting over a temperature range of approximately 1 °C near the isotropization temperature (which is within 3 °C of the T_{NI} of pure 5CB). At concentrations greater than 10 wt % ABASiBB exhibited a single sharp transition with T_{NI} substantially greater than that of pure 5CB.

The solubility of the triblocks differs somewhat from their homopolymer analogs: PBSiCB5 has greater solubility than ABASiCB5 in 5CB but, conversely, PBSiBB was less soluble than ABASiBB. PBSiCB4 and PBSiCB5 were soluble in 5CB in all proportions tested and exhibited a single sharp transition between the isotropic and nematic phases. The biphasic region of PBSiBB solutions was observed to be much more pronounced than that of ABASiBB solutions; approximately 10 °C for all concentrations examined.

4. THERMODYNAMICS OF SELF-ASSEMBLY

A unique feature of triblock copolymer gels in LC solvent is the discontinuous change in solvent quality coincident with the first-order LC phase transitions. The transition from gel to sol takes place over an extremely small temperature range compared to bulk BCPs or physical gels of BCPs swollen with isotropic solvent. The transition is broadened in bulk BCPs due to transient compositional fluctuations [12], and in isotropic gels due to the continuous change in solvent quality with [13, 14] temperature. The enormous sensitivity of LC gels to temperature and polymer concentration allows mechanical properties to be tuned with small changes to these parameters; the elastic modulus of ABASiCB4 gels, for example, increases by an order of magnitude when polymer concentration is increased from 3 to 5 wt % and decreases drastically when temperature is raised from 33 to 35 °C.

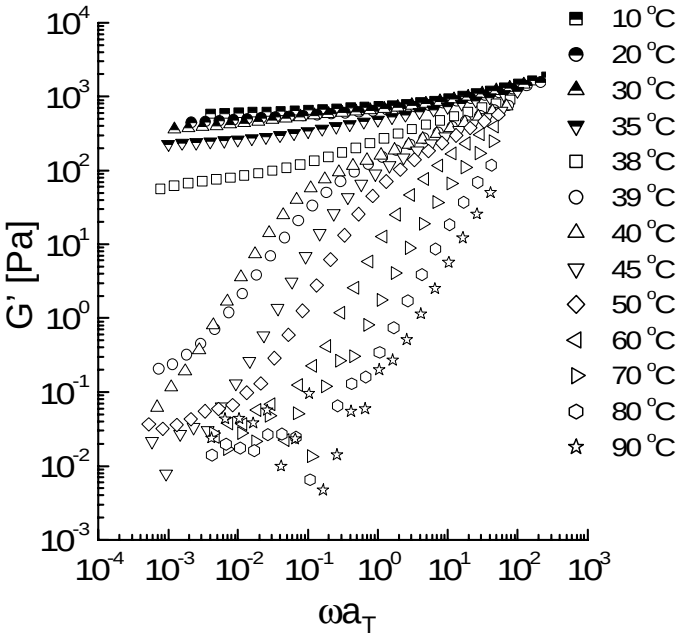

Figure 2: Dynamic storage modulus (G') of 20 wt % ABASiCB5 in 5CB. A plateau modulus is observed below the T_{NI} (38 °C), indicating that the material is a gel. Above the T_{NI} the terminal regime ($G' \sim \omega^{-2}$) is not reached; the material remains thermorheologically complex.

Rheology of the LC gels also reveals an unexpected thermodynamic driving force for their self-assembly. The observation of thermorheological complexity in the isotropic phase of the 20 wt % ABASiCB5 gel is evidence that PS endblock association persists above T_{NI}. We did not expect this because PS homopolymer of a comparable

concentration and molecular weight is soluble in isotropic 5CB [15, 16]. This led us to investigate the phase behavior of solutions of PS homopolymer and SGLCP homopolymer having side-group structure identical to ABASiCB4.

Polystyrene homopolymer (44 kg/mol) was mixed with PBSiCB4 and 5CB in controlled quantities for a total mass of approximately 50 mg then the three components were dissolved together in 100 μL of tetrahydrofuran (THF). Samples were mixed for at least an hour to ensure complete dissolution of all three components. A small drop of the THF solution was placed in the shallow well of an indented microscope slide and the THF was evaporated away at elevated temperature (~100 °C). Slides were examined using a Zeiss optical microscope equipped with a Mettler FP82 hot stage and removable polarizers. Each sample was first heated from room temperature at a rate of 2 °C/min using crossed polarizers to visualize the nematic to isotropic phase transition; the temperature at which the colorful, birefringent texture disappeared was recorded as the isotropization point (T_{NI}). Next, the polarizers were removed and the sample was heated above T_{NI} until droplets characteristic of two-phase, isotropic/isotropic coexistence were no longer observed then cooled at a rate of 10 °C/min. The temperature at which droplets reappeared was recorded as the upper critical solution temperature (UCST). This measurement was repeated five times, examining a different area on the slide each time, and the results averaged.

At temperatures below T_{NI}, ternary mixtures were observed to phase separate into nematic and isotropic phases. Previously established phase diagrams of PS in 5CB [15, 16] show that PS is insoluble in nematic 5CB; mixtures phase-separate into an isotropic, PS-rich phase and a nematic phase nearly devoid of PS altogether. On the other hand, PBSiCB4 is soluble in nematic 5CB at all concentrations we have tested to date (up to 20 wt % polymer)[17, 18]. The measured isotropization points in ternary mixtures (i.e. transition from N+I to I+I biphase or N+I to I) were found to be within 3.5 °C of the bulk T_{NI} of 5CB (35 °C), indicating that the nematic phase contains little or no isotropic diluent and partitioning of the polymers into a PBSiCB4-rich, nematic phase and a PS-rich, isotropic phase must therefore be nearly complete. Nematic 5CB, being a poor solvent for PS, is a strongly selective solvent for PBSiCB4.

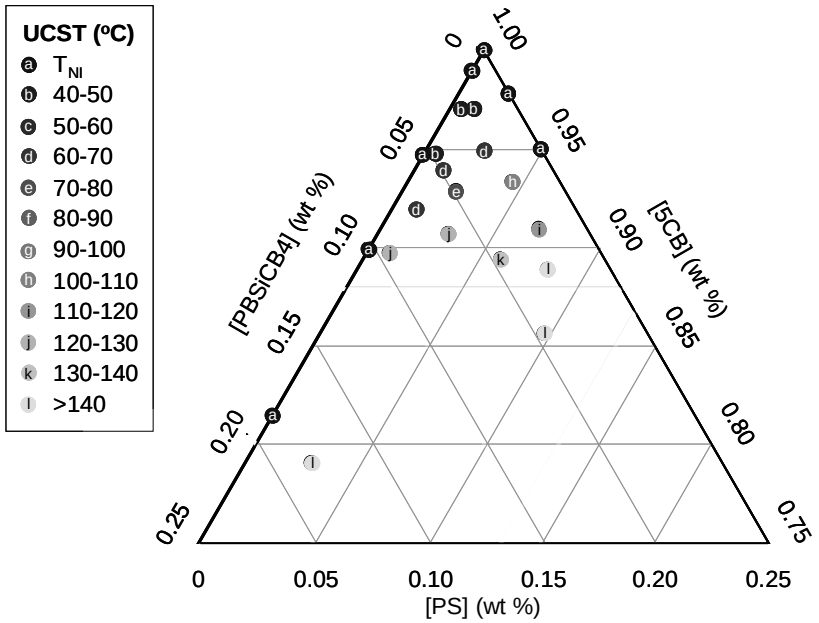

Figure 3: Ternary phase diagram of PS, PBSiCB4, and 5CB determined from optical microscopy. The color of each point expresses the upper critical solution temperature (UCST) at which a single-phase solution is obtained. A UCST of 35 °C means the solution became single-phase immediately upon transitioning to the isotropic phase. A UCST > 140 °C means the mixture began to decompose before a single-phase solution could be observed.

The UCST of ternary blends of PS, PBSiCB4, and 5CB was found to be highly sensitive to the concentrations of the two polymers (Figure 3). An effective solubility limit was quickly reached with increasing concentrations. Binary

solutions of PS with 5CB, or of PBSiCB4 with 5CB, were observed to be single phase above T_{NI}. This result is consistent with previously established phase diagrams of PS with 5CB, which found the two to be miscible above 40 °C, provided the concentration of PS is less than 50 wt % [15, 16], and has been previously reported for solutions of PBSiCB4 [17, 18]. Ternary solutions, on the other hand, exhibited wide miscibility gaps in the isotropic phase. For example, holding the concentration of PBSiCB4 fixed at 4.5 wt % (Figure 4), the addition of 0.5 wt % PS opens up a 14 °C miscibility gap (UCST = 49 °C) which expands to 97 °C (UCST = 132 °C) when the concentration of PS is 6 wt %. When the overall concentration of polymer, PS and PBSiCB4 combined, exceeds approximately 10 wt %, the UCST cannot be reached before the sample thermally degrades, representing an effective solubility limit.

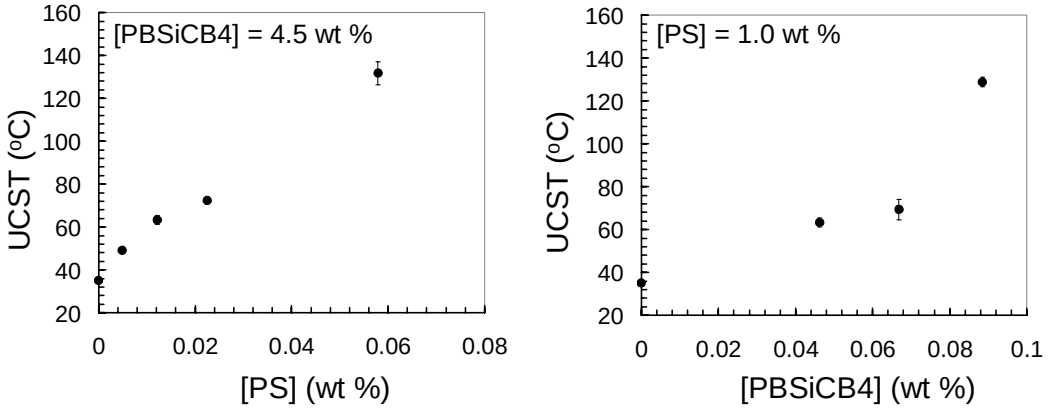

Figure 4: Upper critical solution temperature (UCST) of ternary mixtures of PS, PBSiCB4, and 5CB holding the concentration of PBSiCB4 or PS fixed.

This steep increase in UCST with increasing polymer concentration is surprising because each of the two polymers dissolves in isotropic 5CB alone. Although it is tempting to attribute increasingly large miscibility gaps to unfavorable interactions between the polymers themselves (a large contribution of χ_{AB}), this explanation is unsatisfactory in dilute solutions where polymer-polymer interactions are effectively screened by solvent. Based on the radius of gyration of PBSiCB4 determined using small-angle neutron scattering (SANS), the overlap concentration (c*) is predicted to be approximately 10 wt % at 32 °C. This represents a lower bound on c* for isotropic solutions because the radius of gyration decreases with increased temperature. The overlap concentration of PS, being approximately one tenth the molecular weight, should be much higher than that of PBSiCB4. The majority of our phase diagram (Figure 3) is, therefore, well within a regime where the free energy contribution of χ_{AB} should be negligible.

The observed phase behavior at $c < c^*$ must then be attributable to polymer-solvent interactions and can be explained by the Patterson [19] –Prausnitz [20] treatment of the Scott [21] - Tompa [22] theory for ternary polymer-polymer solutions. Patterson and Prausnitz found that any differential preference of the solvent for one polymer over the other ($\chi_{AS} \neq \chi_{BS}$), even if that preference is small, can induce phase separation. Furthermore, the effect is exacerbated when the molecular weight difference between the polymers is large. Therefore, the observation of phase separation at low concentrations of PS and PBSiCB4 can be attributed to the Patterson-Prausnitz asymmetric solvent effect: the chemical structure of the two polymers is sufficiently different to cause an appreciable difference in polymer-solvent interactions between the two, and the molecular weight ratio of PS to PBSiCB4 is approximately 1:10. We conclude that isotropic 5CB is not a neutral solvent ($\chi_{AS} = \chi_{BS}$) and is better classified as "slightly selective" ($|\chi_{AS} - \chi_{BS}| << \chi_{AS} \approx \chi_{BS}$).

5. SHEAR INDUCED ALIGNMENT

With increasing polymer concentration the mixture forms a gel with as little as a few wt % added polymer. Small amplitude shear experiments confirm gelation of ABASiCB4 at 5 wt % polymer concentration (Figure 5). The storage modulus exhibits a plateau over a significant range of frequencies in which G′ is one order of magnitude greater than G″. The data also illustrate the thermoreversible process of gel formation whereby the polymer is completely solubilized when 5CB is heated to the isotropic state, but the endblocks aggregate when the gel is cooled into the

nematic state. Gelation at low polymer concentrations is enabled by the large molecular weight of the midblock SGLCP. Similar data are collected for a 5 wt % mixture of ABASiCB4 in 5CB and an 18 wt % mixture of ABASiCB5 in 5CB (at lower concentrations ABASICB5 in 5CB phase separates into polymer-rich and polymer-poor phases).

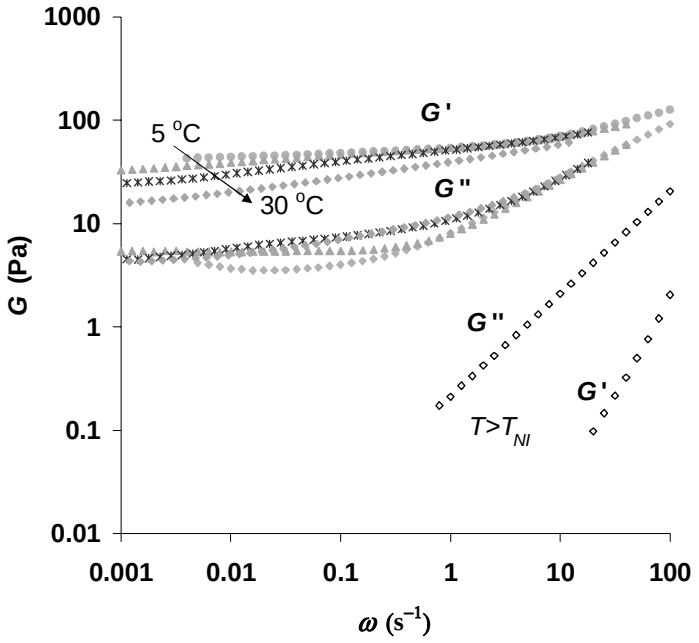

Figure 5: Small amplitude oscillatory shear of 5 wt % ABASiBB in 5CB in a cone and plate rheometer. The T_{NI} is approximately 35.0°C

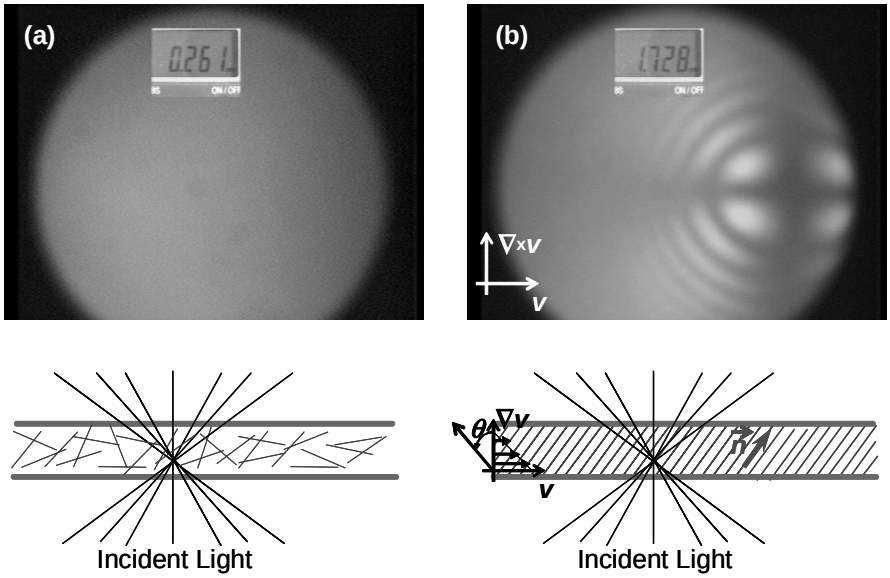

Figure 6: Conoscopic images of 20 wt % ABASiCB5 gel, 400 µm thick, in 5CB at 25°C. The gel before shear (a) and immediately after cessation of shear (b). The cross section schematics illustrate how light interacts with the corresponding polydomain (a) and single-crystal-like (b) orientation of the director.

Alignment methods applicable to SGLCP melts [23] are also applicable to our gels. The gel readily responds to shear, electric fields, magnetic fields, and alignment surfaces. Each of these methods can induce a macroscopic monodomain. High amplitude oscillatory shear at temperatures near the nematic-isotropic transition temperature (T_{NI}) aligns the gels even in a large gap (Figure 6), which cannot be accomplished using surface anchoring.

Magnetic fields and electric fields can align the gel if the gel is cooled slowly from the isotropic state. Uniform alignment via polyimide or SiO_2 coated surfaces requires a small (<10 μm) gap and several days of annealing.

6. STRIPE DEFORMATION IN LC GELS

Finkelmann and coworkers discovered that nematic rubber elasticity manifests itself by the formation of stripe domains when the elastomer is stretched perpendicular to the initial director alignment.[24] These arise because the director is free to rotate within the material to relieve elastic stresses caused by stretching. When the present liquid crystalline gels are constrained between parallel plates, cooling the gel results in a similar striped domain texture in which stripes run perpendicular to the initial director (Figure 7). The texture reversibly disappears and reappears when the gel is heated and then cooled, and the critical temperature for stripe formation depends both on the gap thickness and polymer concentration. Stripes do not appear when the gel is too thin. In the case of a 5% ABASiBB gel, stripes do not appear in 4 and 9 μm thick cells, but they do appear in 13 and 16 μm thick cells (Table 2). For gels of higher polymer concentration, stripes appear even in thin cells, but a greater degree of frustration (lower temperature) is required for smaller gaps. In the case of a 10% gel, the transition temperature for a 4μm cell is 28 °C compared to 31 °C for a 9 μm thick cell. Also, gels with a greater polymer concentration more readily show the striped texture. 10% gels display stripes at all gap thicknesses tested while 5% gels show stripes only for gaps 13 μm or greater. Stripe formation is thus favored in larger gaps and more concentrated gels. The pitch length of the stripes depends on the gap thickness and the polymer concentration but is independent of temperature. The pitch is observed to increase with increasing gap, and decreasing the polymer concentration decreases the pitch.

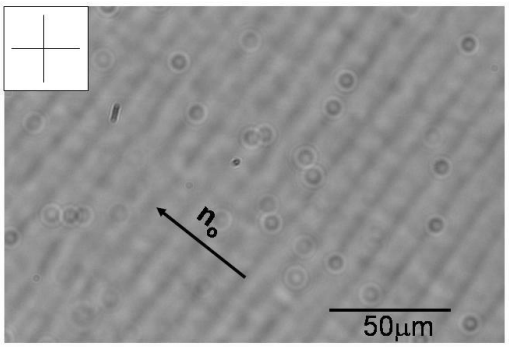

Figure 7: Polarized optical micrograph of a 10% ABASiBB polymer gel in a 9 μm gap at 20.0 °C. The orientation of the director imprinted during crosslinking denoted by the arrow in the figure is perpendicular to the stripes, and the orientation of the crossed polars is shown in the top left-hand corner of the image.

The striped state represents a periodic modulation of the director from an initially uniformly aligned state, which arises due to the presence of a crosslinked polymer network. A side-chain liquid crystalline polymer dissolved in a nematic solvent adopts an anisotropic chain conformation coupled to the nematic order of the solvent.[25] Due to the dependence of the nematic order on temperature, the chain anisotropy depends on the temperature. Based on prior literature on nematic elastomers[1] we expect that an unconstrained free standing gel would change shape: in the case of a strongly prolate alignment tendency (e.g. SiBB), the gel would expand in the direction of director orientation with decreases in temperature (our gel is too soft to carry out the same experiment). When constrained between glass plates, however, expansion of the gel in the direction of increasing anisotropy is prevented by the boundary conditions, and the gel

becomes increasingly frustrated as the temperature decreases. At a critical temperature, the gel "buckles" by deforming and rotating the director periodically; a periodic displacement field is coupled to the director field in the gel (Figure 8). This deformation is a soft-elastic deformation that includes local shear, as in the stripe domains in nematic elastomers. This buckling partially relieves the tension of the frustrated polymer network while at the same time satisfying the macroscopic boundary conditions imposed by the substrates.

Polymer Concentration (wt %)	Gap Thickness (μm)	Transition Temperature (^{o}C)	Stripe Size (μm)
10	14.6	N/A	12
10	9	31 +/- 1	11
10	4	28 +/- 1	7
5	16	N/A	17
5	13	N/A	15
5	9	No Stripes Observed	
5	4	No Stripes Observed	

Table 2: Details of striped texture, from POM, for ABASiBB gels. We were unable to measure an accurate transition temperature in the larger gaps.

In collaboration with Bob Meyer and Guangnan Meng we have developed a simple model to treat the onset of buckling. It correctly captures the following trends. 1) These bands occur in materials having very low modulus, which explains why thermal and electric-field induced bands have not been observed in prior elastomers and gels and why they vanish with increasing polymer concentration in the present systems. 2) The tendency to form bands depends on the degree of orientational coupling between the backbone and the mesogens, which explains why bands are more readily induced when the SGLCP strands are strongly prolate type (SiBB), than when they are weakly oblate (SiCB4). 3) The decrease of the band pitch with increasing modulus (e.g., increasing concentration). 4) The decrease of pitch with decreasing gap thickness.

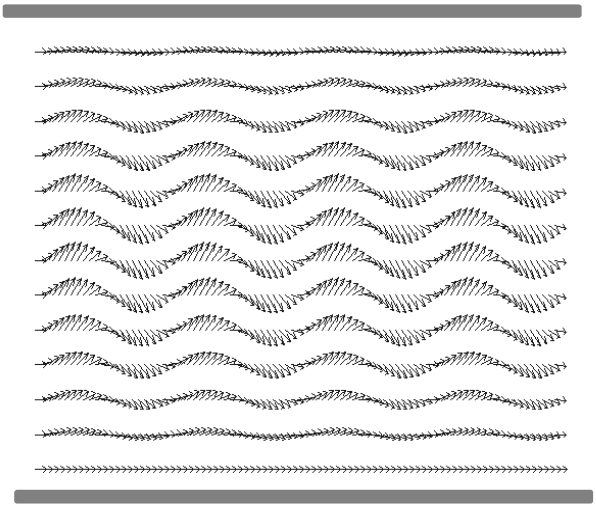

Figure 8: Schematic of the director orientation in the stripe-deformed state of the gel. The amplitude of the distortion is greatest in the center of the cell, where the aligning effects of the substrate is minimal. The director rotation is shown perpendicular to the substrate, but in general the deformation may also involve rotation within the plane as well.

7. ELECTRO-OPTIC BEHAVIOR

The transient electro optic behavior of gels in the polydomain state is similar to that of polymer stabilized liquid crystals (PSLCs) in that the solvent reorients and the polymer provides a memory of the initially unaligned state.[26] However, while in PSLCs the polymer matrix consists of thick, phase separated polymer bundles insensitive to external fields, in our gels the solubilized network can reorient in response to applied fields (Figure 9). Upon removal of the electric field, elastic stresses drive the rotation of the liquid crystal molecules to return to the direction dictated by the SGLCP midblock. Relaxation is independent of the applied field for pure liquid crystals and PSLCs. On the other hand, in LC gels relaxation time increases with the amplitude of the field for fields greater than 2.0V/μm. We hypothesize that large fields drive reorganization of the polymer network; therefore, relaxation following exposure to large fields couples to the much slower process of exchange of nematophobic endblocks among the physical junctions of the network.

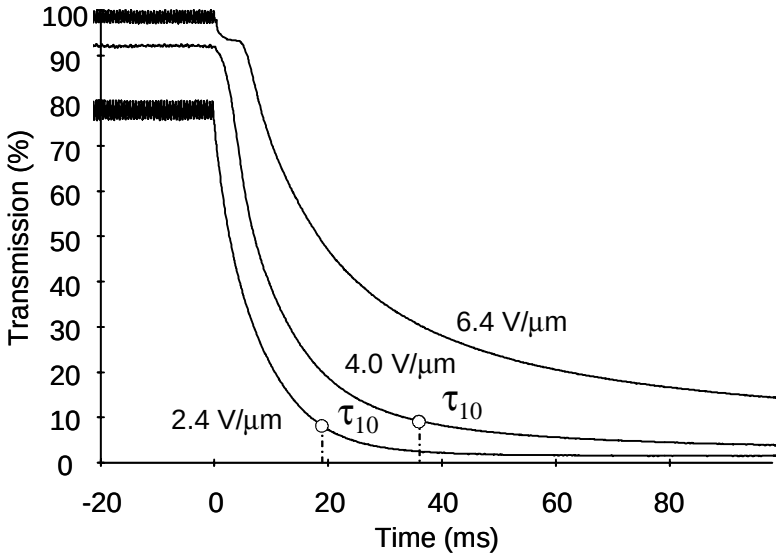

Figure 9: Measured transmission as a function of time for a 25 μm thick layer of 5 wt % ABASiBB following the removal of AC fields at 1,000 Hz. The time required to return to 10 % of the maximum transmittance is denoted τ_{10}. At the highest field of 6.4 V/μm the τ_{10} of 170 ms is beyond the scale of the graph.

8. SUMMARY

The present approach to creating liquid crystalline gels is sufficiently general to open the way to a broad range of materials that combine liquid crystalline order and dynamics with polymer self assembly and elasticity. In the future it may be possible to create dilute gels having chiral nematic order, such that the combination of rapid response and optical uniformity of self-assembled LC gels can be harnessed for tunable wavelength filters and lasers.[6] The ease of alignment of the polymer within these gels may provide facile routes to align currently intractable chiral smectic liquid crystals, such as those exhibiting analog response with excellent speed. The ability to systematically adjust the interplay of polymeric and director orientation and motion through precise control of the polymer concentration, SGLCP length between crosslinks, and the nature of the small molecule LC in the gel provides molecular insight into the physical properties of LC gels, guiding rational design for diverse technological applications. The exceptional electro-optic and mechano-optic responsiveness of these gels coupled with their unique thermal sensitivity suggests they would be ideal

candidates for use in large-area printable display technology. A solution of triblock copolymer in LC solvent could be heated just above T_{NI} to transform the material into a liquid amenable to ink-jet printing. Gelation will spontaneously occur subsequent to printing by simply allowing the solution to cool to room temperature, and the desired alignment state can be achieved by mechanical shear. Alternatively, these block copolymers could be utilized as rheology modifiers to facilitate large-area coating of LC materials; adding as little as 1 wt % polymer can significantly enhance the viscosity of the LC without adversely affecting switching speed.

REFERENCES

1 M. Warner and E. M. Terentjev, *Liquid Crystal Elastomers* (Clarendon, Oxford, 2003).
2 M. Warner and E. M. Terentjev, Progress in Polymer Science **21**, 853 (1996).
3 R. A. M. Hikmet, Journal of Applied Physics **68**, 4406 (1990).
4 W. Lehmann, H. Skupin, C. Tolksdorf, et al., Nature **410**, 447 (2001).
5 M. Moriyama, S. Song, H. Matsuda, et al., J. Mater. Chem. **11**, 1003 (2001).
6 H. Finkelmann, S. T. Kim, A. Munoz, et al., Advanced Materials **13**, 1069 (2001).
7 S. V. Fridrikh, E. M. Terentjev, and M. Warner, J. Phys. II **7**, 1059 (1997).
8 M. L. Auad, M. D. Kempe, J. A. Kornfield, et al., Manuscript in Preparation (2003).
9 V. P. Shibaev, S. G. Konstromin, and N. A. Plate, Eur. Polym. J. **18**, 651 (1982).
10 S. Lecommandoux, M. F. Achard, F. Hardouin, et al., Liquid Crystals **22**, 549 (1997).
11 J. D. Laffitte, M. F. Achard, F. Hardouin, et al., Liquid Crystals **17**, 487 (1994).
12 G. H. Fredrickson and F. S. Bates, Annu. Rev. Mater. Sci. **26**, 501 (1996).
13 K. Inomata, D. Nakanishi, A. Banno, et al., Polymer **44**, 5303 (2003).
14 T. Sato, H. Watanabe, and K. Osaki, Macromolecules **33**, 1686 (2000).
15 H. Hakemi, Polymer **40**, 4099 (1999).
16 H. Hori, O. Urakawa, and K. Adachi, Macromolecules **37**, 1583 (2004).
17 M. D. Kempe, N. R. Scruggs, R. Verduzco, et al., Nature Mateials **3**, 177 (2004).
18 R. Verduzco, N. R. Scruggs, M. Kempe, et al., Manuscript in Preparation (2005).
19 L. Zeman and D. Patterson, Macromolecules **5**, 513 (1972).
20 C. C. Hsu and J. M. Prausnitz, Macromolecules **7**, 320 (1974).
21 R. L. Scott, The Journal of Chemical Physics **17**, 279 (1949).
22 H. Tompa, Trans. Faraday Soc. **45**, 1142 (1949).
23 C. B. Mcardle (Ed.), *Side Chain Liquid Crystal Polymers* (Chapman and Hall, New York, 1989).
24 H. Finkelmann, I. Kundler, E. M. Terentjev, et al., J. Phys. II France **7**, 1059 (1997).
25 M. Kempe, J. A. KORNFIELD, and J. LAL, Macromolecules **37**, 8730 (2004).
26 I. Dierking, Advanced Materials **12**, 167 (2000).

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